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TECHNICAL NOTE 2030

VARIATION WITH TEMPERATURE OF SURFACE
TENSION OF LUBRICATING OILS

By Sydney Ross

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SUMMARY

Surface-tension measurements from room temperature to 180°C of a series of aeronautical lubricating oils and a few liquids of associated interest are reported. The measurements were obtained from a Du Nouy tensiometer and corrected according to the theory of Harkins and Jordan. The critical temperatures of the liquids are calculated and thus a general classification of existing oils into three groups is provided. The effect of use or exposure to high temperatures is to leave the relation between surface tension and temperature virtually unchanged, unless the use has been excessively prolonged, when decomposition begins and the surface tension is lowered.

INTRODUCTION

Among the properties most intimately connected with the foaming of lubricating oils is their surface tension. Part of the work conducted in these laboratories has therefore been the determination of the variation of surface tension with temperature. In the present report no attempt is made to derive any relation between foaming properties and surface tensions; the data on surface tensions are put on record for their own intrinsic interest.

This work was conducted at Stanford University under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

SYMBOLS

γ	surface tension, dynes per centimeter
R	radius of ring measured from center of ring to center of wire
r	radius of wire

V	volume of liquid raised above free surface of liquid
F	correction factor applied to surface-tension equation; a function of R^3/V and R/r
M	molecular weight of liquid
ρ	density of liquid
t_{cr}	critical temperature of liquid, °C

APPARATUS AND PROCEDURE

The Cenco-Du Nouy ring tensiometer was used, observing the precautions stipulated by Harkins and Jordan (reference 1). All the observed readings were corrected by the method described by Harkins and Jordan (reference 1).

The sample is first heated to about 180° C and readings of the surface tension are made continuously during the course of cooling down to room temperature.

The variation of surface tension of some oils has already been reported by Mills (reference 2). Mills used the capillary-rise method, which is not so useful as the ring method during the course of cooling of the sample because of uncertainty about the temperature of the liquid inside the capillary. The accuracy of the capillary-rise method is usually, but by no means always, conceded to be superior to that of the ring method. Mills' measurements were made with an accuracy of 0.2 dyne per centimeter. A comparison of Mills' results for mineral oils with the present results for Aeroshell 120 and NACA Reference Oil shows an agreement within the limits of experimental error:

Oil	Surface tension at -		
	20° C	54° C	99° C
Mills' results; capillary-rise method			
Mineral oil (a)	32.3	29.8	26.6
Mineral oil (b)	32.3	29.8	27.1
Stanford results; ring method			
Aeroshell 120	32.5	29.9	26.4
NACA Reference Oil	32.9	30.3	26.8

CORRECTIONS TO SURFACE-TENSION READINGS

In 1926, Harkins, Young, and Cheng (reference 3) determined the correct equation for the application of the ring method to the measurement of surface tension.

$$\gamma = \frac{Mg}{4R} \times f\left(\frac{R^3}{V}, \frac{R}{r}\right)$$

or

$$\gamma = \frac{Mg}{4R} F$$

The experimentally determined values of F , the correction factor, are given for different values of R/r by Harkins and Jordan (reference 1).

The readings here reported were obtained from an instrument whose ring has a value of $R/r = 39.5$. The corrections to be subtracted from the observed reading are of the order of 2.5 dynes per centimeter when a liquid of density 0.9 gram per cubic centimeter (e.g., lubricating oil) is being measured.

RESULTS

The relation between the temperature t and the surface tension γ of a normal or nonassociated liquid is represented by the Ramsay-Shields - Eötvös equation (see references 4 and 5)

$$\gamma\left(\frac{M}{\rho}\right)^{2/3} = 2.12(t_{cr} - 6^\circ - t) \quad (1)$$

where M is the molecular weight, ρ the density, and t_{cr} the critical temperature.

According to this equation a completely linear relation between γ and t is not to be expected, except through a relatively small temperature range, because of the variation of the density with temperature.

For lubricating oils, which are multicomponent systems, the relation between t and γ is unpredictable. However, on the basis

of experimental results, it is found that for most oils the change in surface tension between 20° C and 110° C can be fairly accurately represented by a straight line. Where this is the case, the line can be extrapolated to a temperature where the surface tension is zero, which is the critical temperature. As it is obvious from the experimental curves that there is a marked deviation from the linear relation at higher temperatures, it is unlikely that the value of t_{cr} found by such a procedure is the true critical temperature. But it does give an experimentally determined value that has a relative significance in comparing one lubricating oil with another.

A list of values of t_{cr} obtained as described above for a series of existing oils, new and used, as well as for some other liquids, is given in table I.

DISCUSSION

When arranged in order of decreasing value of t_{cr} it is found that the oils are thereby grouped according to types; the 120-grade oils together occupy the center of the list, two nonhydrocarbon liquids occur above them, and the lighter mineral oils occur below them. A solution of 0.5 percent lead Aerosol OT in Squibb mineral oil has the value of t_{cr} considerably displaced, whereas a solution of Span 40 in mineral oil does not affect the surface-tension characteristics. It is also found that Syntholube has its place along with the 120-grade oils while Standard Synthetic Oil is grouped with the light mineral oils.

The slope of the linear part of the curve of γ against t is a function of the average molecular weight and density. Table I includes also the values of the slope, calculated by means of the expression

$$m = \frac{\gamma_{100} - \gamma_{25}}{75}$$

For the paraffin hydrocarbons (according to reference 6) the value of $\frac{d\gamma}{dt}$ becomes 0.07 as the carbon chain increases to about 30 carbon atoms. The value 0.08, found here for most lubricating oils, corresponds to about 17 to 18 carbon atoms had the chain been straight.

The diagrams (figs. 1(a) to 1(f)) do not represent all the data obtained but are for graphic representation of differences in surface tension caused by the use of the oils or by materials dissolved in them.

It can be seen that in most cases prolonged heating or use of an oil results in a general lowering of its surface tension throughout the entire temperature range from 25° C to 180° C. This lowering may amount to only a few tenths of a dyne per centimeter in some cases up to as much as 2 dynes per centimeter where the oil has been considerably decomposed. In those latter cases it is to be anticipated that many foam inhibitors will be relatively less effective or may have to be used in larger amounts.

Stanford University

Stanford University, Calif., July 31, 1945

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TABLE I.- SURFACE TENSION AND ITS TEMPERATURE COEFFICIENT
FOR EXISTING LUBRICATING OILS

Oil sample	Surface tension at -		$-100\left(\frac{\gamma_{100} - \gamma_{25}}{75}\right)$	t_{cr} (°C)
	25° C	100° C		
Glycerol	60.9	53.5	9.87	642
0.5 percent lead Aerosol OT in Squibb mineral oil	29.5	24.7	6.40	486
Castor oil	35.6	29.7	7.87	477
Gulf Airline	32.35	26.7	7.53	455
California oil; dewaxed, solvent-treated		27.0	7.64	453
NACA Reference Oil	32.5	26.7	7.73	445
McClellan Field used oil; engine grade 120		26.9	7.87	442
McClellan Field new oil; engine grade 120		27.2	8.0	440
Intava 1 AA-120; new oil	32.8	26.85	7.93	439
California Cold Test Distillate (Union Oil)		27.75	8.19	439
Sinclair 120; new oil	32.5	26.55	7.93	435
Aeroshell 120	32.2	26.3	7.87	434

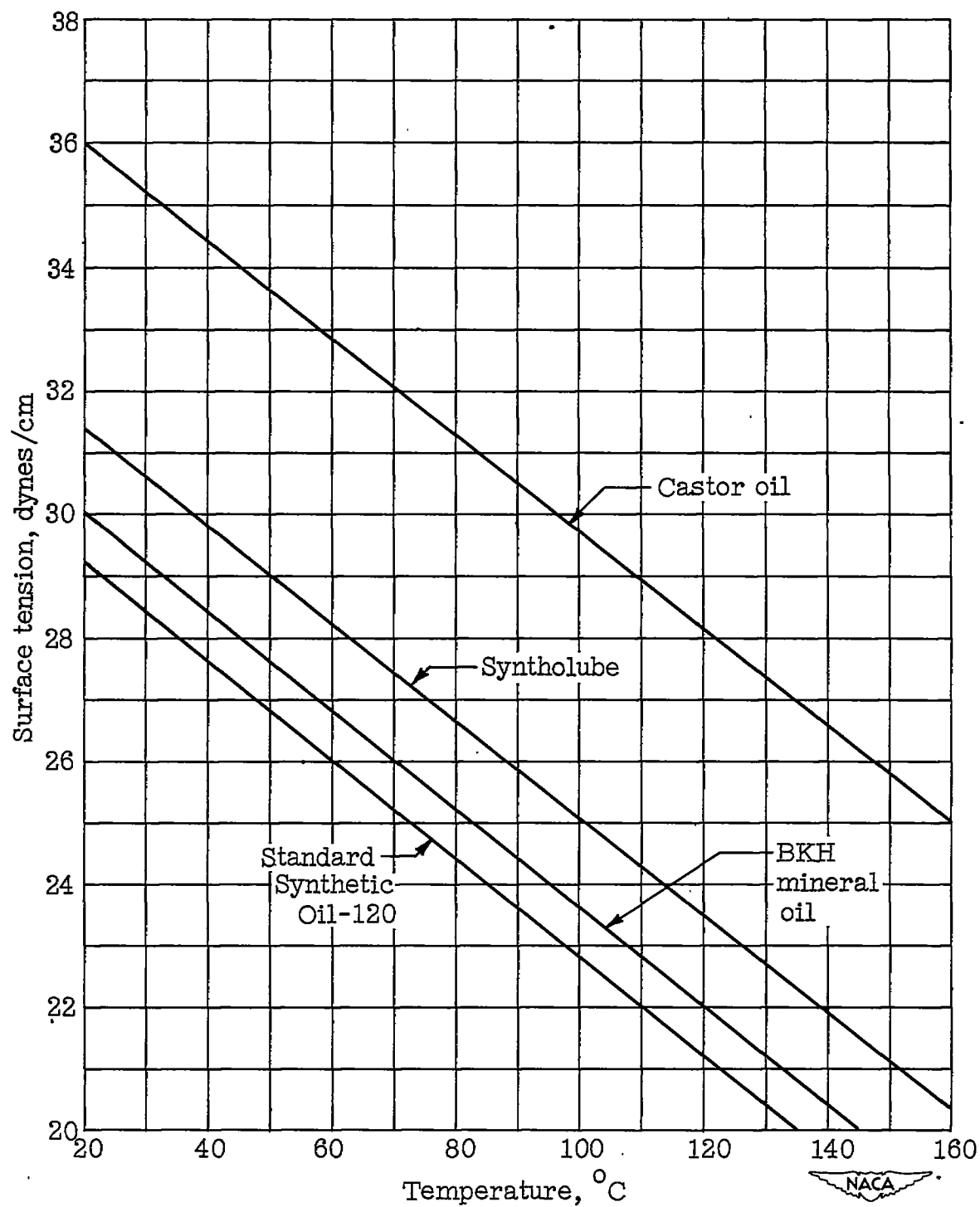


TABLE I.- SURFACE TENSION AND ITS TEMPERATURE COEFFICIENT

FOR EXISTING LUBRICATING OILS - Concluded

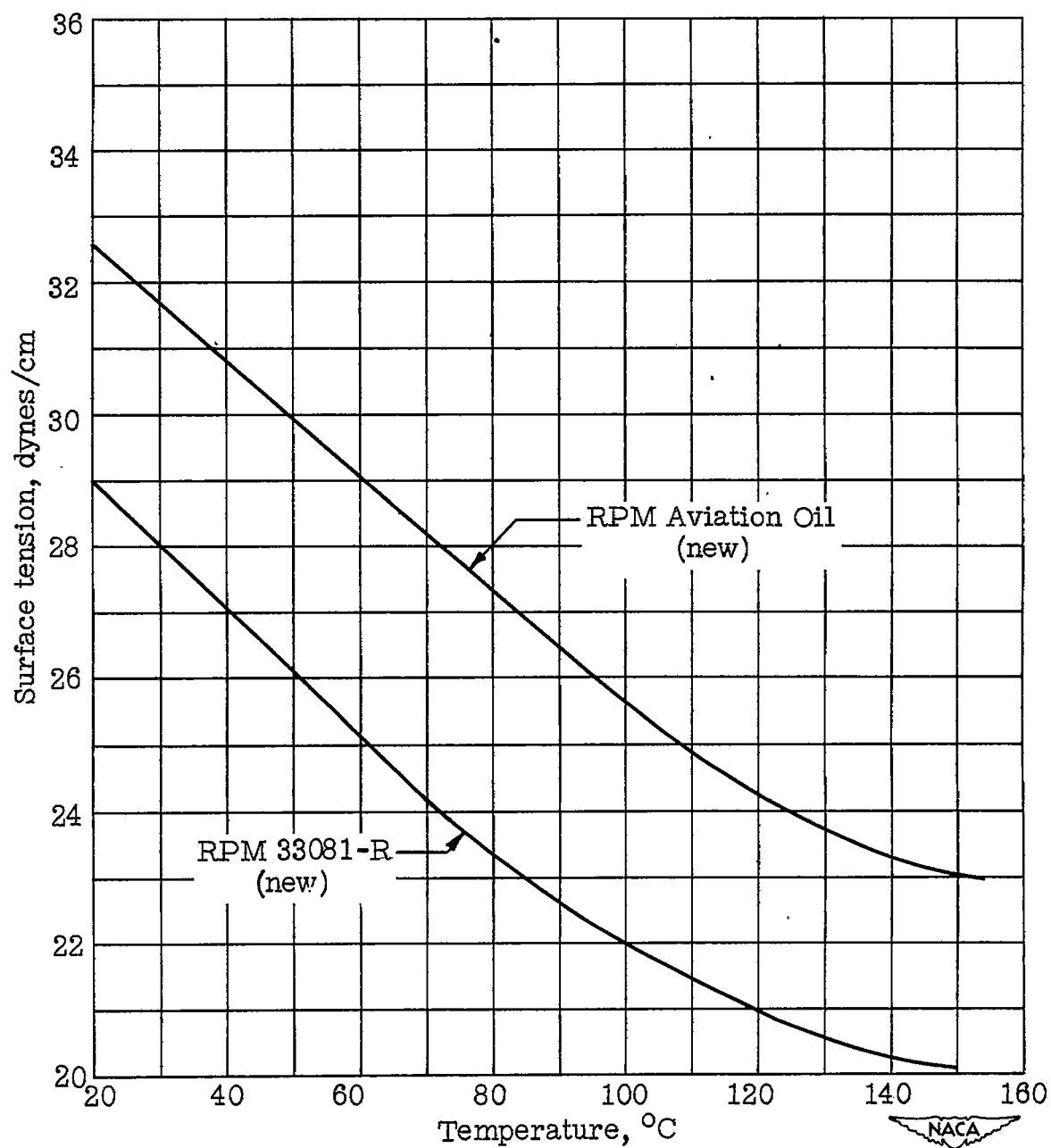
Oil sample	Surface tension at -		$-100\left(\frac{\gamma_{100} - \gamma_{25}}{75}\right)$	t_{cr} (°C)
	25° C	100° C		
Sinclair 120; used oil	32.5	26.5	8.00	431
Texaco 120	32.3	26.2	8.13	422
Shell Formula 2	32.2	26.1	8.13	421
Triton 40		26.1	8.13	421
Syntholube	31.0	25.05	7.93	416
Gilmore Oil; new	32.4	26.14	8.35	413
Gilmore Oil; used	32.4	26.14	8.35	413
Intava 748; used for 40 hours at 270° F		26.1	8.67	401
BKH mineral oil	29.6	23.65	7.93	398
BKH mineral oil plus Span 40 (saturated solution)	29.6	23.6	8.00	395
Squibb mineral oil	31.6	25.2	8.53	395
Standard Synthetic Oil	28.9	22.8	8.13	380





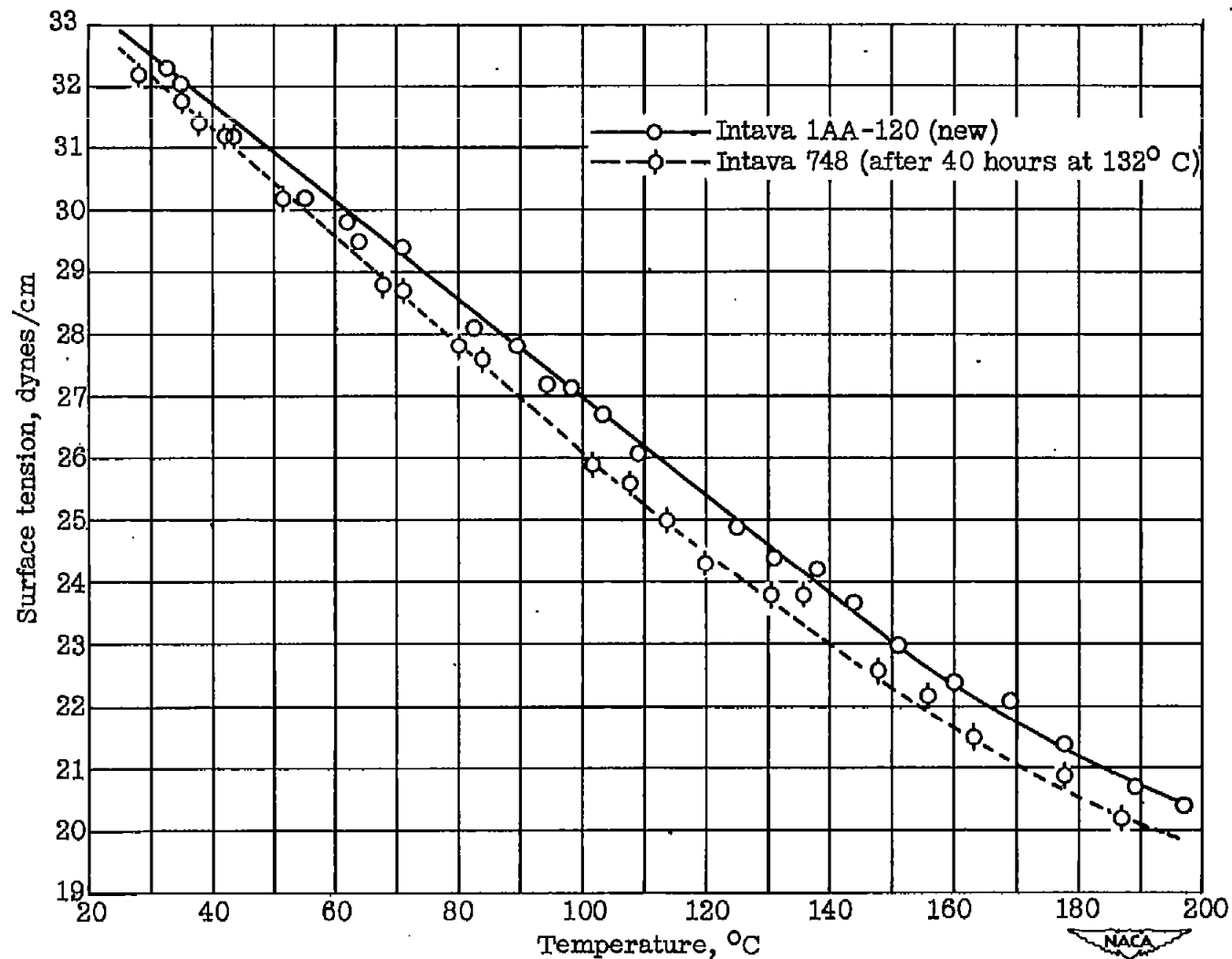
(a) Castor oil, Syntholube, Standard Synthetic Oil-120, and BKH mineral oil.

Figure 1.- Relation between surface tension and temperature for a series of lubricating oils.



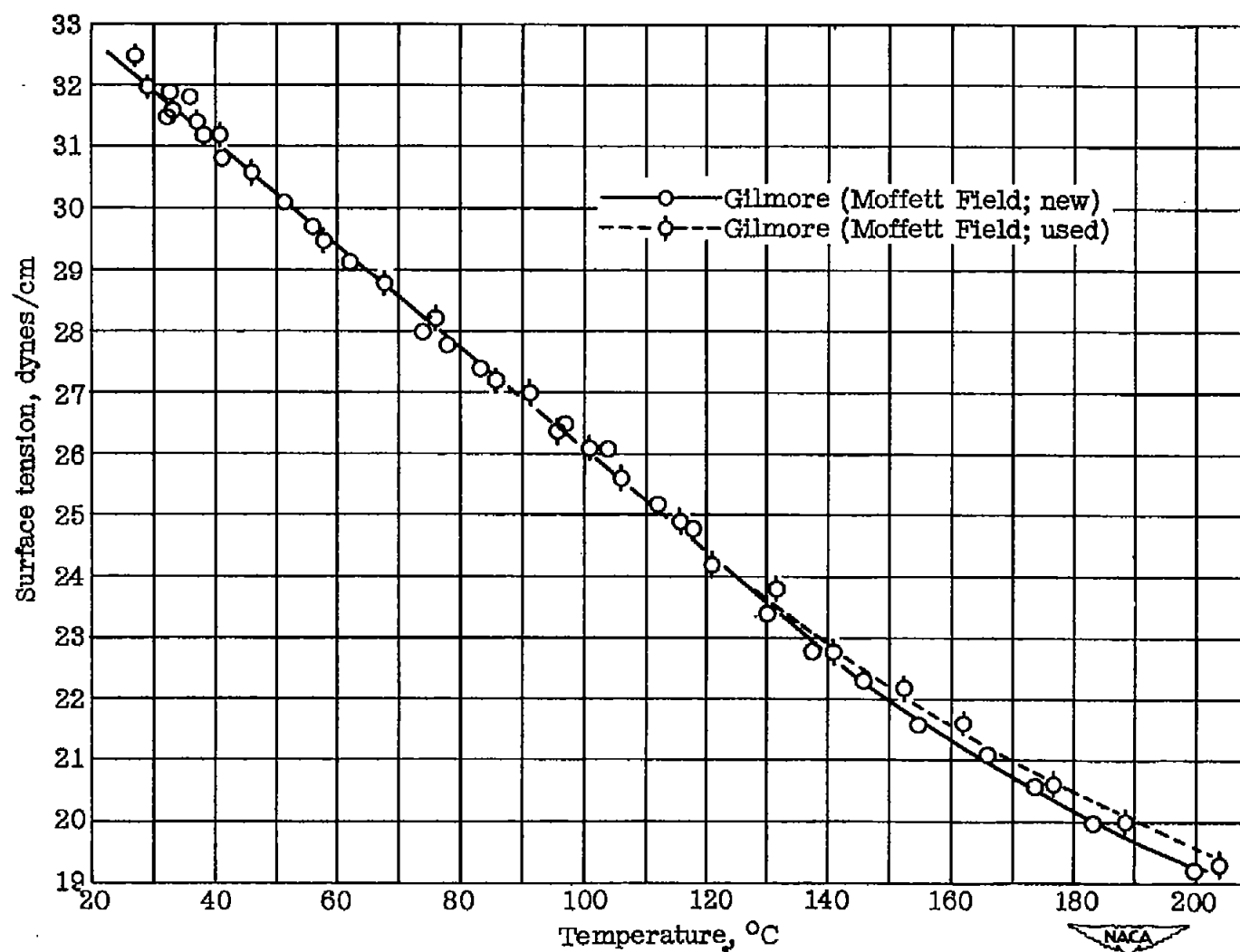
(b) RPM aviation oil (new) and RPM 33081-R (new).

Figure 1.- Continued.



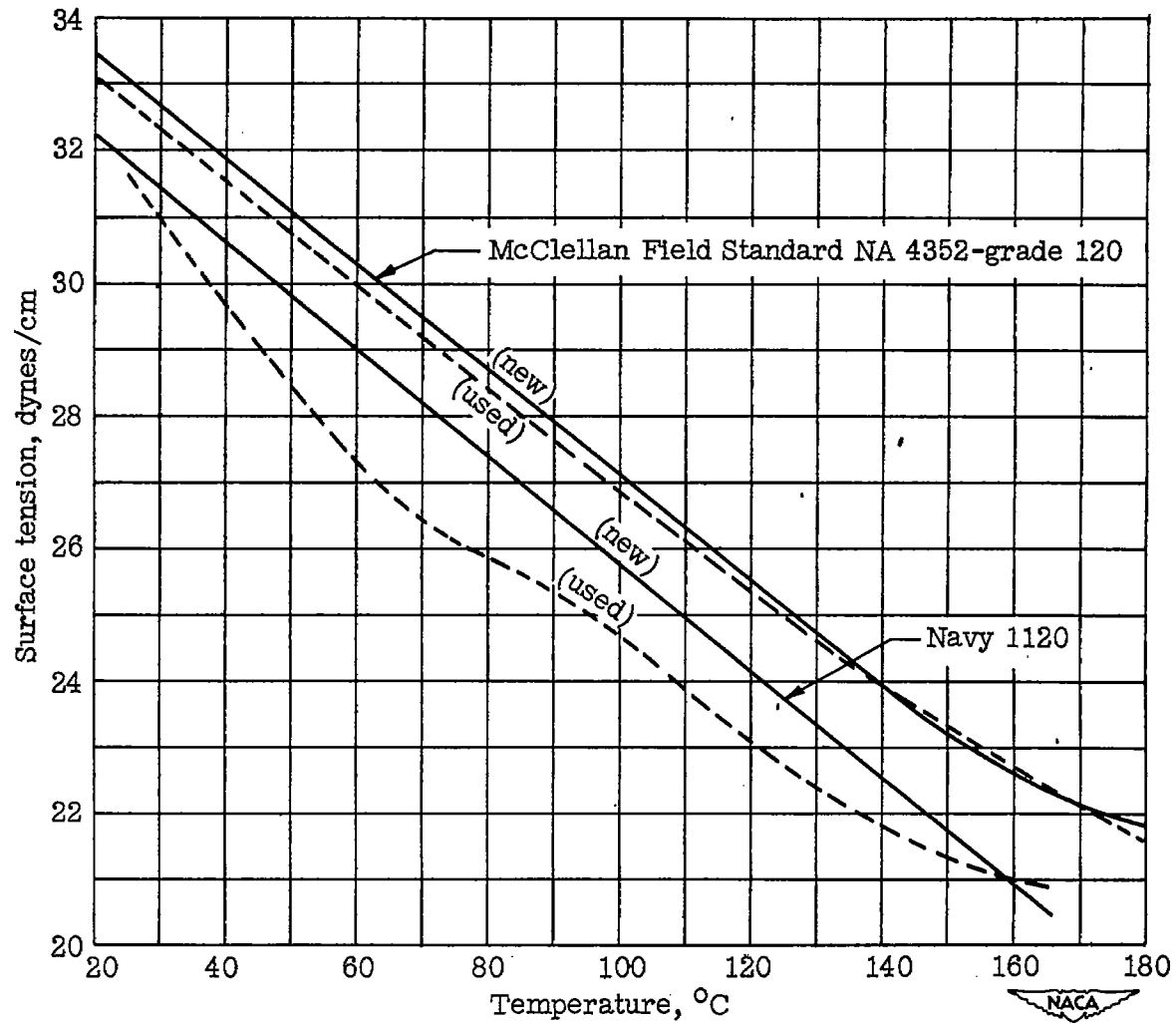
(c) Intava 1AA-120 (new) and Intava 748 (after 40 hours at 132° C).

Figure 1.- Continued.



(d) Gilmore (Moffett Field, new) and Gilmore (Moffett Field, used).

Figure 1.- Continued.



(f) McClellan Field Standard NA 4352, grade 120 and Navy 1120.

Figure 1.- Concluded.